

# PATENT SPECIFICATION

NO DRAWINGS

Inventors: THOMAS RAYMOND GRIFFITH and DONALD WESLEY MACGREGOR



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## COMPLETE SPECIFICATION

### Improved Vulcanizable Composition

We, NATIONAL RESEARCH COUNCIL, a Canadian Body Corporate, of Sussex Drive, Ottawa 2, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in the formulation of rubber vulcanizates and in particular to new useful vulcanizates containing active fillers, which adversely affect vulcanization.

In the past the use of active material as filler in compounding or formulation of rubber has not been desirable because of the deleterious effect on the curing rates caused by the presence of active filler. Certain attempts have been made to overcome this difficulty by reducing the activity prior to compounding with the rubber. For example, there has been described a method of using certain active silicious materials as filler, which method requires pretreatment of the active material with alkali so as to reduce the adsorptive capacity. However, for certain specific uses it is known to be an advantage to retain the activity of the filler in the rubber. For example, active carbon is at present used in tires having white side walls, the active carbon being in a layer immediately adjacent the white side wall. The active carbon provides a barrier layer which picks up coloured material or material that may become coloured upon exposure to sunlight, thus preventing discolouration of the white side wall. The amount of active carbon presently used in this way is however not sufficient to adversely effect the vulcanization. Active carbon is also useful in connection with non-staining reclaimed rubber where it acts as an adsorbent of materials in the reclaim that might cause discolouration. Apart from such specific uses of active filler in rubber, this in-

vention is an important contribution to the art of rubber formulation in that it extends the list of materials useful as fillers. Each filler imparts to rubber a peculiar combination of physical properties that is difficult to duplicate with other fillers so that any new filler added to the list of useful materials is of importance to the art.

New and useful rubber compositions have been obtained by the present invention according to which we provide a vulcanizable composition comprising rubber and a filler active in the presence of an organic accelerator and sulphur to retard the normal vulcanization rate of a rubber composition and a minor quantity of at least one oxide of lead, copper or bismuth the filler being added to the rubber in the dry state. The vulcanizable composition of the present invention corresponds substantially exactly to ordinary rubber except for the presence of the active filler and the modifier which coats therewith to offset the known adverse effects of such a filler as discussed hereinabove. It has been found that the modifier also acts in some manner not well understood to enhance physical properties of the vulcanizate to a surprising degree.

As particular embodiments of our invention, we have found that the active filler may be activated powdered carbon such as "Darco G-60" (Registered Trade Mark) or "Nuchar" (Registered Trade Mark). The "Darco G-60" is a product made by heat treatment of lignite and charcoal and the "Nuchar" is a product made by heat treatment of lignin. Useful active filler has also been found in carbon residue obtained by the heat treatment of lignosol (calcium lignin sulphonate). The ground residue has a pronounced activity and when compounded with rubber retards the vulcanization to a marked extent. As a result of our experimentation, it is believed that the delaying

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effect is caused by the presence of excess hydrogen sulphite during vulcanization. Hydrogen sulphide is known to retard vulcanization even in the presence of powerful organic accelerators, although it is probably a necessary intermediate in the vulcanization reaction. It is thought that the hydrogen sulphite combines with the rubber molecule at a double bond, and in doing so splits into a sulphydryl group and hydrogen. The cross linkage between the rubber molecules is then completed with the formation of a sulphur bridge by reaction of two sulphydryl groups to split out hydrogen sulphide. If the concentration of hydrogen sulphide in the vulcanization medium is too high the evolution of  $H_2S$  by the latter reaction will be retarded, and the vulcanization delayed.

Certain silicious materials e.g. Santocel (Registered Trade Mark) and Bentonite also delay vulcanization.

The materials which we have found to be effective as modifiers in the formation of rubber containing active fillers may generally be described as compounds which are capable of reacting with the hydrogen sulphide under the conditions of vulcanization. As indicated hereinabove, the particular materials which we have found to be of use include certain metal oxides, which oxides are at least slightly soluble in aqueous alkali, and the sulphides of the metals concerned will precipitate in the presence of  $H_2S$  from dilute hydrochloric acid and are substantially insoluble in sodium polysulphide. Metal oxides of this type include litharge, red lead, brown lead, cupric oxide and bismuth

trioxide.

As has been indicated hereinabove the method of compounding the vulcanizates of the present invention presents no new problems to the art. One can start with smoked sheet in the usual way or one can start alternatively with raw latex. In using raw latex for example the rubber is precipitated with acid and milled until a homogeneous mass is formed. The active filler along with the required modifier and usual ingredients such as sulphur, accelerators and activators are then blended in to give the vulcanizable composition. The actual vulcanization is carried out in the conventional manner at temperatures in the neighbourhood of  $250^\circ$  to  $320^\circ F$ .

The active fillers are incorporated in the desired amount which may vary within quite wide limits. A content of about 50% by weight based on the rubber content may be taken as an optimum amount, but there could conceivably be as little as 5% or as much as 250%, in each case based on the weight of the rubber. The amount of modifier which is useful has also been found to lie within quite wide limits and for convenience is calculated as a percentage of the amount of filler used. An optimum amount of modifier has been found to be from about  $12\frac{1}{2}\%$  to about  $17\frac{1}{2}\%$  by weight; however as little as 1% has been found to be of some benefit and the practical maximum has been found to be about  $37\frac{1}{2}\%$ .

The present invention will be understood more completely from a consideration of specific examples discussed hereinbelow.

TABLE I

	Ordinary Acceleration			Litharge Acceleration		
	A	B	C	D	E	F
Smoked sheet	100	100	100	100	100	100
"DARCO G-60" activated carbon	50	—	—	50	—	—
"NUCHAR", activated carbon	—	50	—	—	50	—
"SANTOCEL", activated silicious material	—	—	50	—	—	50
Phenyl-beta-naphthylamine, antioxidant	1	1	1	1	1	1
Stearic acid	2	2	2	2	2	2
Pine tar	5	5	5	5	5	5
Zinc oxide	5	5	5	3	3	3
Litharge	—	—	—	7	7	7
Zinc dimethyldithiocarbamate, accelerator	—	—	—	1	1	1
<i>N</i> -cycloHexyl-2-benzothiazolesulphonamide, accelerator	—	—	—	0.5	0.5	0.5
Mercaptobenzothiazole, accelerator	1.5	1.5	1.5	—	—	—
Sulphur	2	2	2	2	2	2
Cure:	30 min. at 282° F.			30 min. at 282° F.		
	A	B	C	D	E	F
Stress at 300% p.s.i.	No cure	No cure	290	1090	—	470
Tensile strength p.s.i.	"	"	810	1245	1440	920
% Elongation at break	"	"	730	330	220	660
Shore hardness	"	"	52	62	66	53

A number of vulcanizates were compounded according to the formulations set forth in Table I. The improved nature of the vulcanizates made according to the present invention is readily apparent. In the case of formulations represented by A and B, it is seen that no cure was obtained, but substantially the same formulations, represented by D and E, which included litharge were readily cured and gave a vulcanizate with improved properties.

Experiments have also been made to test the effectiveness of other metal oxides such as copper and bismuth. In each case similar

beneficial effects were measurable when these materials were used along with active filler in the rubber formulations.

Thus it will be realized that the present invention provides useful and novel compositions having properties of value in many uses mentioned hereinabove. In addition the improved characteristics of the novel compositions will allow their use in many ways not heretofore possible.

#### WHAT WE CLAIM IS:—

1. A vulcanizable composition comprising rubber and a filler active in the presence of an

- organic accelerator and sulphur to retard the normal vulcanization rate of a rubber composition and a minor quantity of at least one oxide of a metal selected from the group consisting of lead, copper and bismuth, the filler being added to the rubber in the dry state.
- 5 2. A vulcanizable composition according to claim 1 wherein oxide is present in an amount of from about 1% to about  $37\frac{1}{2}\%$  by weight
- 10 of said filler.
3. A vulcanizable composition according to claim 1 or 2 wherein oxide is present in an amount of from about  $12\frac{1}{2}\%$  to about  $17\frac{1}{2}\%$  by weight of said filler.
4. A vulcanizable composition as claimed in any of the preceding claims wherein the filler is an activated carbon or an active silicious material.
5. Vulcanizable compositions and vulcanizes substantially as herein described.
- 15 20 NATIONAL RESEARCH COUNCIL,  
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